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(54) **PROCESS FOR TANNING AND TANNING AGENT**

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PROCEDE DE TANNAGE ET AGENT TANNANT

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Description

[0001] The present invention relates to a process for the mineral tanning of unpickled pelts with chromium salts without increasing the basicity of the liquor using low molecular weight polyols as penetration auxiliaries.

[0002] The one-bath process, which comprises steps for pickling, tanning with chromium salt and increasing the basicity, has become established in tanning with mineral salts. In pickling, the animal hide digested and degreased in the beamhouse is treated with strong acids, for example sulphuric acid or formic acid, and salts, for example sodium chloride. With this treatment, the degree of association of the carboxyl groups in the collagen is reduced so that the animal hide has a high pH below 2. In this pH range, the fixing of the chromium salt is greatly reduced and the permeation of the salts is increased. In addition, for improving the penetration, the chromium salts can be masked with organic carboxylic acids. The tanning effect is then developed by increasing the pH to about 3.5 to 6. For this purpose, alkaline compositions are added (for example, magnesium oxide or sodium carbonate) when increasing the basicity of the liquor, in amounts such that the optimum value for tanning is established. For this method of tanning, chromium salts have a Schorlemmer basicity of at least 30%. Fungicides, which likewise penetrate into the pelts and have to disperse in order to provide sufficient protection against fungal attack, particularly if the hide is split, are often added to the liquors. In the one-bath process, the tanning is carried out in the pickling bath.

[0003] For this form of tanning, large amounts of chemicals are required, leading to the high level of wastewater pollution. The residual content of, for example, chromium salts in the liquor requires an aftertreatment for reducing the content in the wastewater. Improvements have therefore been proposed for increasing the liquor exhaustion and reducing the consumption of chemicals, in order to meet ecological requirements and to increase the cost-efficiency.

[0004] US-A-4,715,861 recommends treating pickled pelts or pelts during the pickling first with aldehyde acids or keto acids, for example glyoxalic acid, in order to increase the exhaustion of the liquor and to decrease the consumption of chromium salt. The steps of pickling and of increasing the basicity are, however, still required. Aldehyde acids and keto acids are physiologically unsafe and require special safety measures. The action of the aldehyde acids and keto acids consists in reaction with amino groups of the collagen, leading to an increase in the acidity of the pelt and hence better chromium absorption.

[0005] EP-A-0 822 263 describes a process for tanning with chromium salts, in which pelts are treated with 3-hydroxybutyraidehyde and pickling and increasing the basicity are dispensed with. By reaction of the aldehdye groups with amino groups of the collagen, the isoelectric point is reduced so that chromium salts penetrate sufficiently and an increase the basicity is superfluous. WO 00/66793 discloses the same process with α- or β-hydroxyaldehydes. The compositions used for the pretreatment are volatile compounds which can be handled in tanneries only with difficulty. Furthermore, aldehydes are physiologically unsafe. The use of these processes requires particular safety apparatuses, which, from economic points of view, eliminates the advantages of dispensing with pickling and increasing the basicity.

[0006] The published Brazilian Patent Application PI 0004258-7 A discloses chromium complexes of chromium salts and oligomeric masking compositions having a low Schorlemmer basicity of from 10 to 20%. They are suitable for the tanning of pelts without pickling and increasing the basicity. The required penetration is achieved by the low basicity, these compositions for tanning being capable of penetrating only slowly because their molecular weights are too high and therefore being unconvincing.

[0007] WO 95/13400 describes a composition for the tanning of pelts which contains water as a carrier, a chromium salt, brine and a long-chain alkylpolyglucoside and has a pH of from 1 to 3. The alkylpolyglucoside is intended to improve the permeation. Owing to the molecular size and the surfactant structure, however, the effect is not very pronounced. For tanning, the basicity of the liquor must be increased after the penetration of the chromium salts.

[0008] CZ-A-8188-88 describes solid or aqueous, stabilized formulations of basic chromium salts which contain a polyol, such as, for example, sugar or glycerol, as a stabilizer. Bases, such as, for example, MgO or $NaHCO_3$, must be added to the formulations for increasing the basicity (self-basification). Nothing is mentioned about an improvement in the penetration, in particular on separate addition of chromium salt and polyol, and avoidance of pickling and increasing of the basicity.

[0009] Processes for the direct tanning of pelts from the beamhouse have not become established, owing to the existing disadvantages, although said tanning is truly desirable because of the ecological and economic advantages.

[0010] It has now surprisingly been found that the existing disadvantages can be avoided and faster and uniform penetration and a higher absorption of basic chromium salts in the pelt and hence also a higher exhaustion of the liquor are achieved, outstanding through tanning of the pelts and hence very good physical properties (for example tensile strength, ultimate tensile strength, stitch tear resistance) are achieved, the salt consumption (for example sodium chloride) is reduced, pickling and increasing the basicity are avoided and the time required for complete tanning is reduced and moreover at the same time outstanding penetration and distribution of simultaneously used fungicide are achieved if the pelts are treated with an effective amount of a polyol during the tanning.

[0011] The invention firstly relates to a process for tan-

ning of unpickled pelts and without increasing the basicity of the liquor by the action of basic chromium(III) salts in an aqueous liquor, which is characterized in that

(a) either an effective amount of at least one nonsaccharide, aliphatic polyol is added to the aqueous liquor, the pelt is pretreated and then the chromium salt is added and allowed to act, or
(b) an effective amount of at least one aliphatic, nonsaccharide polyol and a basic chromium salt are added separately but simultaneously to the liquor and allowed to act on the pelt.

[0012] Pelts are understood as meaning degreased and digested hides (if the skin was unhaired) and skins prepared in the beamhouse for tanning.

[0013] The process variant (a) is preferred according to the invention. In the process variant (b), polyol and chromium salt can be added all at once or in portions.

[0014] Chromium salts for tanning have long been known and are commercially available as solid or liquid formulations. They are salts of trivalent chromium with mineral acids, the sulphates having become established in practice. The products available are generally mixtures of chromium trioxide and alkali metal sulphates, such as, for example, sodium sulphate. The basicity, which is stated as a percentage according to Schorlemmer, is adjusted by means of the mixing ratio. Here, a basicity of 0% is assigned to pure chromium trisulphate and a basicity of 100% to pure chromium trihydroxide. Intermediate forms, such as, for example, $Cr(OH)SO_4$, have a basicity of 33.3%. The chromium salts can be masked in a manner known per se with aliphatic mono- or dicarboxylic acids and are preferably unmasked.

[0015] The chromium salts used in the process according to the invention preferably have a Schorlemmer basicity of from 15 to 50%, more preferably from 25 to 50%, particularly preferably from 30 to 45% and very particularly preferably from 30 to 42%.

[0016] In the context of the invention, nonsaccharide means that the aliphatic polyols are not sugars. In the process according to the invention, sugars do not have the effect of the aliphatic polyols and can therefore be used only additionally as fillers or extenders.

[0017] The aliphatic polyols are preferably of low molecular weight and preferably have molecular weights of not more than 1 000, more preferably not more than 500, particularly preferably not more than 300 and very particularly preferably not more than 150.

[0018] The aliphatic polyols to be used according to the invention may contain from 2 to 20, preferably from 2 to 10 and particularly preferably from 2 to 8 carbon atoms and optionally oxygen atoms, and from 2 to 12, preferably from 2 to 6, particularly preferably from 2 to 4 hydroxyl groups. They may be soluble or emulsifiable in water. Particularly preferably, the aliphatic polyols contain altogether from 2 to 8 carbon atoms and optionally oxygen atoms and from 2 to 4 hydroxyl groups. The aliphatic groups to which hydroxyl groups are bonded may be derived from linear or branched alkanes, cycloalkanes, mono- or dialkylcycloalkanes having hydroxyl groups bonded to the alkyl groups, dialkylbenzene having hydroxyl groups bonded to the alkyl groups, O-heterocycles (for example tetrahydrofuran, oxacyclohexane or dioxane), mono- or dialkyl-O-heterocycles having hydroxyl groups bonded to the alkyl groups, and polyoxaalkylenediols. The rings of cyclic polyols may be unsubstituted or substituted by C_1-C_4-alkyl or C_1-C_4-alkoxy.

[0019] The alkanes may be, for example, ethane and the isomers of propane, butane, pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, tridecane, tetradecane, pentadecane, hexadecane, heptadecane, octadecane, nonadecane and eicosane. The aliphatic polyols based on alkanes are preferably diols, triols and tetrols:

[0020] Examples of diols are those of the formula HO-C_nH_{2n}-OH, in which n is a number from 2 to 20, preferably from 2 to 12 and particularly preferably from 2 to 6. Some specific examples are ethylene glycol, 1,2-or 1,3-propylene glycol, 1,2-, 1,3-and 1,4-butylene glycol, 1,2-, 1,3-, 1,4- and 1,5-pentylene glycol, 1,2-, 1,3-, 1,4-, 1,5- and 1,6-hexylene glycol, 1,2-, 1,3-, 1,4-, 1,5-, 1,6- and 1,7-heptylene glycol, 1,2-, 1,3-, 1,4-, 1,5-, 1,6-, 1,7- and 1,8-octylene glycol, nonylene glycol, decylene glycol, undecylene glycol, tetradecylene glycol, hexadecylene glycol and octadecylene glycol.

[0021] The triols may correspond to the formula $(HO)_2$-$C_nH_{2n-1}OH$, in which n is a number from 3 to 12 and preferably from 3 to 8. Specific examples are 1,2,3-propanetriol, 1,2,3- or 1,2,4-butanetriol, 1,2,3-, 1,2,4-, 1,2,5- or 2,3,5-pentanetriol, 1,2,3-, 1,2,4-, 1,2,5-, 2,3,5-, 1,3,6-or 1,2,6-hexanetriol, 1,4,7-heptanetriol, 1,4,8-octanetriol, trihydroxymethylmethane, 1,1,1-trihydroxymethylethane and 1,1,1-trihydroxymethylpropane.

[0022] The tetrols may correspond to the formula $(HO)_2$-$C_nH_{2n-2}(OH)_2$, in which n is a number from 4 to 12 and preferably from 4 to 8. Specific examples are 1,2,3,4 tetrahydroxybutane, 1,2,3,5-tetrahydroxypentane, 1,2,3, 6-tetrahydroxyhexane, 1,2,6,8-tetrahydroxyootane and tetrahydroxymethylmethane (pentaerythritol).

[0023] The cycloalkanes may be those having 3 to 12 and preferably 5 to 8 carbon atoms in the ring. Some specific examples are cyclopentane-1,3-diol, cyclohexane-1,3- or -1,4-diol and cyclooctane-1,2-, -1,3- or -1,4-diol.

[0024] In the mono- or dialkylcycloalkanes having hydroxyl groups bonded to the alkyl groups, the cycloalkane ring preferably contains from 3 to 12 and particularly preferably from 5 to 8 carbon atoms in the ring. The alkyl groups contain preferably from 1 to 4 and particularly preferably 1 or 2 carbon atoms. Some specific examples are 1-hydroxymethylcyclopentan-3-ol, 1-hydroxymethylcyclohexan-4-ol, 1-hydroxyethylcyclopentan-3-ol, 1-hydroxyethyl-cyclohexan-4-ol, 1,3-dihydroxymethylcyclopentane, 1,4-dihydroxymethylcyclohexane, 1,3-dihydroxyethylcyclopentane, 1,4-dihydroxyethylcyclohexane

and 1-hydroxymethyl-4-hydroxyethylcyclohexane.

[0025] In the dialkylbenzene having hydroxyl groups bonded to the alkyl groups, the alkyl groups contain preferably from 1 to 4 and particularly preferably 1 or 2 carbon atoms. Some specific examples are 1,3- or 1,4-dihydroxymethylbenzene, 1,3- or 1,4-dihydroxyethylbenzene and 1,1-hydroxymethyl-4-hydroxyethylbenzene.

[0026] Some examples of polyols of O-heterocycles are 2,3-dihydroxytetrahydrofuran and 3,4-dihydroxy-1-oxacyclohexane.

[0027] Examples of mono- or dialkyl-O-heterocycles having hydroxyl groups bonded to the alkyl groups are 2-hydroxy-3-hydroxymethyltetrahydrofuran, 3-hydroxy-4-hydroxymethyl-1-oxacyclohexane, 2,3-dihydroxymethylterahydrofuran and 3,4-dihydroxymethyl-1-oxacyclohexane.

[0028] The polyoxaalkylenediols may correspond, for example, to the formula $HO-(R-O)_xH$, in which R is 1,2-propylene and preferably ethylene and x is a number from 2 to 12 and preferably from 2 to 4. Some examples are diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol and mixed polyoxaalkylenediols, such as, for example, ethylene 1,2-propylene ether glycol.

[0029] According to the invention, the polyols also include those cyclic polyols in which some or all of the hydroxyl groups bonded to the ring have been etherified with hydroxyalkyl, preferably hydroxyethyl.

[0030] The polyols may be used as an individual component or as a mixture of at least two polyols.

[0031] The polyols can be used alone or in combination with monoethers of glycol. In this case, mixtures of such monoethers with polyols or the individual components may be added to the liquor. The amount of the components in the mixture may be, for example, from 10 to 70% by weight, preferably from 20 to 60% by weight and particularly preferably from 30 to 50% by weight of monoether and from 90 to 30% by weight, preferably from 80 to 40% by weight and particularly preferably from 70 to 50% by weight of polyol.

[0032] The monoethers of glycols may be, for example, those of the formula C_1-C_{12}-, preferably C_1-C_8- and particularly preferably C_1-C_4-alkyl-O-(C_m-H_{2m})-OH, in which m is a number from 2 to 12, preferably from 2 to 8 and particularly preferably from 2 to 4. The monoethers of glycols may also be, for example, those of the formula C_1-C_{12}-, preferably C_1-C_8- and particularly preferably C_1-C_4-alkyl-$(O-C_yH_{2y})_z$-OH, in which y is a number from 2 to 6 and preferably 2 or 3 and z is a number from 2 to 6 and preferably 2 or 3. Examples of the group -C_mH_{2m}- are ethylene, 1,2- or 1,3-propylene, 1,2-, 1,3- and 1,4-butylene, 1,2-, 1,3-, 1,4- and 1,5-pentylene, 1,2-, 1,3-, 1,4-, 1,5- and 1,6-hexylene, 1,2-, 1,3-, 1,4-, 1,5-, 1,6- and 1,7-heptylene, 1,2-, 1,3-, 1,4-, 1,5-, 1,6-, 1,7- and 1,8-octylene, nonylene, decylene, undecylene and dodecylene. The alkyl group may be linear or branched alkyl, for example methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, pentyl and hexyl.

[0033] Some specific examples of monoethers of glycols are ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monopropyl ether, ethylene glycol monobutyl ether, 1,2- or 1,3-propylene glycol monomethyl ether, 1,2- or 1,3-propylene glycol monoethyl ether, 1,2- or 1,3-propylene glycol monopropyl ether, 1,2- or 1,3-propylene glycol monobutyl ether, butylene glycol monomethyl ether, butylene glycol monoethyl ether, butylene glycol monopropyl ether, butylene glycol monobutyl ether, diethylene glycol monomethyl or monoethyl ether, triethylene glycol monomethyl or monoethyl ether and di-1,2-propylene glycol monomethyl or monoethyl ether.

[0034] The pH of the liquor at the time of addition of products to be used according to the invention may be, for example, from 3 to 8, preferably from 3.5 to 6 and particularly preferably from 3.5 to 4.5. The pH is adjusted by adding acids, for example formic acid, and amounts of sodium chloride which are reduced compared with the pickling. In the case of chromium salts of low basicity, for example from 15 to about 25, the pH of the liquor is preferably in the neutral to slightly basic range since these chromium salts impart to the liquor an acidic pH sufficient for the tanning. At higher basicfies of the chromium salts, for example from about 20 to 25% or higher, the pH is advantageously in the slightly acidic range.

[0035] The amount of chromium salts in the liquor may be, for example, from 1 to 8% by weight and preferably from 1.5 to 5% by weight of chromium trioxide (Cr_2O_3), based on the weight of the pelt. In the tannery, the amount is usually calculated on the basis of the theoretical content of chromium trioxide.

[0036] Even in small amounts, the polyol acts in the desired manner. The minimum amount of polyols is, for example, 0.1% by weight, based on the weight of the pelts. The addition of larger amounts can be avoided since no further substantial improvement can be achieved. The upper limit may be 20 and preferably 10% by weight. More preferably, the amount is from 0.5 to 5% by weight and particularly preferably from 0.5 to 2% by weight. Combinations of glycols with monoethers can be used in amounts such that the glycol component is present in the abovementioned amounts in the liquor.

[0037] It has also surprisingly been found that fungicides which are required for protection against fungal attack penetrate considerably better into the pelt with the use of the polyols, and effective protection can therefore be achieved with smaller amounts. It is therefore advantageous concomitantly to use a fungicide in the process stage (a) or (b). The amount may be from 0.01 to 5% by weight and preferably from 0.1 to 3% by weight, based on the weight of the pelts. Fungicides for this purpose are known and commercially available. Some examples are 2-(thiocyanomethylthio)benzothiazole, 2-octyl-2H-isothiazol-3-one, 4,5-dichloro-2-octyl-2H-isothiazol-3-one, zinc bis-(2-pyridinethiol-1-oxide), zinc pyrothione and 3-iodo-2-propynylbutyl carbamate.

[0038] The polyols may be added directly to the liquor,

or mixtures of the polyols with fungicides may be added. The polyols may also be added as a mixture with a chromium salt and optionally additionally a fungicide if the mixtures are prepared immediately before use without heating.

[0039] In the process of the present invention mixtures of

(a) a basic chromium(III) salt for the tanning of pelts,
(b) a nonsaccharide, aliphatic polyol and
(c) a fungicide can be used.

[0040] In the mixture, the amount of chromium(III) salts may be, for example, from 30 to 95% by weight, preferably from 40 to 90% by weight and particularly preferably from 40 to 80% by weight, the amount of the polyol may be from 70 to 5% by weight, preferably from 60 to 10% by weight and particularly preferably from 60 to 20% by weight and the amount of the fungicide may be from 0.1 to 5% by weight and preferably from 1 to 3.5% by weight, the percentages by weight summing to 100.

[0041] In the process of the present invention mixtures of

(a) a nonsaccharide, aliphatic polyol and
(b) a fungicide can be used.

[0042] In the mixture, the amount of aliphatic polyol may be from 90 to 99% by weight and preferably from 97 to 99% by weight and the amount of the fungicide may be from 10 to 1% by weight and preferably from 3 to 1% by weight. The mixtures according to the invention may additionally contain water, for example up to 50% by weight and preferably up to 35% by weight, based on the total mixture.

[0043] The preparation of the mixtures can be carried out in a simple manner by mixing the components by means of known methods. However, it is also possible to provide ready-made mixtures. Known methods are likewise used for this purpose. Depending on the consistency and amounts of the components, it is possible to prepare powders or granules by dissolving or dispersing the components, optionally in an inert solvent, precipitating the components and then drying them, or spray-drying the solutions or dispersions.

[0044] It is furthermore possible, depending on the amounts used, to fill the components into containers and deliver them to the tanneries in this form.

[0045] In the process of the present invention also a kit consisting of two or three containers which each contain

(a) a basic chromium salt for the tanning of pelts and a nonsaccharide, aliphatic polyol, or
(b) a nonsaccharide, aliphatic polyol and a fungicide, or
(c) a basic chromium salt of the tanning of pelts, a nonsaccharide, aliphatic polyol and a fungicide can be used.

[0046] The invention furthermore relates to the use of at least one nonsaccharide, aliphatic polyol for improving the penetration of basic chromium salts and optionally additionally of fungicides in the tanning of unpickled pelts in acidic, aqueous solution.

[0047] The process according to the invention can be carried out in such a way that washed pelts are introduced into water, a salt is added to the liquor, for example sodium chloride, and an acid is then added, for example formic acid. The pH in the liquor is adjusted thereby. Thereafter, either the aliphatic polyol can be added and allowed to act on the pelt or the polyol and the chromium salt can be added simultaneously. The pretreatment may last from about 30 minutes to 2 hours. After the pretreatment, the chromium salt is added and can be allowed to act, for example, for from about 2 to 10 hours. With simultaneous addition, the treatment time may be from about 2.5 to 10 hours. The process is carried out at from room temperature to 50°C and preferably up to 45°C. After the tanning, the leather obtained is washed and is ready for further processing.

[0048] The following examples explain the invention in more detail.

A) Preparation of mixtures

Example A1: Mixture of polyol and fungicide

[0049] 150 g of α-D-glucose are stirred in 150 g of water at 50°C for 20 minutes in order to dissolve the glucose completely. The temperature is reduced to 30°C and 700 g of 1,2-propanediol (water content 0.2%) are added and stirring is effected for 10 minutes. Thereafter, 3% of 2-(thiocyanomethylthio)benzothiazole (TCMTB) are added and stirring is effected for a further 5 minutes. A brownish liquid is obtained.

Example A2: Mixture of polyol and chromium salt

[0050] 30 g of α-D-glucose is added at 50°C to 100 g of water and stirred until completely dissolved. The temperature is reduced to 30°C and thereafter 200 g of propane-1,2-diol (water content about 0.2%) are added and stirring is effected for 10 minutes. 680 g of aqueous chromium salt solution [chromium(III) sulphate ($Cr(OH)SO_4$; 33% basicity in Schorlemmer units and 15% of Cr_2O_3)] are then added and stirring is effected for a further 10 minutes. A green viscous liquid is obtained.

Example A3: Mixture of polyol, chromium salt and fungicide

[0051] 30 g of α-D-glucose is added at 50°C to 100 g of water and stirred until completely dissolved. The temperature is reduced to 30°C and thereafter 200 g of propane-1,2-diol (water content about 0.2%) are added and

stirring is effected for 10 minutes. 680 g of aqueous chromium salt solution [chromium(III) sulphate ($Cr(OH)SO_4$; 33% basicity in Schorlemmer units and 15% of Cr_2O_3)] and 10% of 2-(thiocyanomethylthio)benzothiazole were then added and stirring is effected for a further 10 minutes. A green viscous liquid is obtained.

B) Use examples

[0052] Stated percentages are percent by weight, based on the amount of the pelt.

Example B1:

[0053]

a) 100 g of α-D-glucopyranosyl-β-D-fructofuranoside were added at 30°C to 400 g of water and stirred until completely dissolved (about 20 minutes). 500 g of ethylene glycol (water content about 0.2%) were then added and stirring is effected for a further 10 minutes. A colourless and slightly viscous product is obtained.

b) 40% of water are added to 50 kg of pelt (Swiss bulls) in a drum, 4% of sodium chloride are added and a waiting period of 10 minutes is allowed. Thereafter, 0.5% of formic acid is added and the pelt is treated for one hour. 1% of the mixture according to a) is then added and allowed to act on the pelt for 1.5 hours. The pH of the liquor is 4.5. 6% of chromium sulphate having a basicity of 33% is then added and tanning is effected for 6 hours. A further 1% of sodium chloride is then added and treatment is effected overnight. Heating to 44°C is then effected and the liquor is kept at this temperature for 12 hours. The pH is then 3.8-3.9. The liquor is discharged and the tanned hide is washed with water. The hide has been completely tanned. The liquor contains only 0.15% of chromium.

Example B2:

[0054]

a) 150 g of α-D-Glucose is added at 50°C to 150 g of water and then stirred until completely dissolved. The temperature is reduced to 30°C and 700 g of 1,2-propanediol (water content about 0.2%) are added and stirring is effected for a further 10 minutes. A colourless and slightly viscous product is obtained.

b) 40% of water are added to 500 kg of pelt (Ukrainian cows) in a drum, 4% of sodium chloride are added and a waiting period of 10 minutes is allowed. Thereafter, 0.5% of formic acid is added and the pelt is treated for one hour. 1.5% of the mixture according to a) is then added and allowed to act on the pelt for 1.5 hours. The pH of the liquor is 4.0. 6% of chromium sulphate having a basicity of 33% is then added and tanning is effected for 6 hours. Heating to 44°C is then effected and the liquor is kept at this temperature for 12 hours. The pH is then 3.8-3.9. The liquor is discharged and the tanned hide is washed with water. The hide has been completely tanned. The liquor contains only 0.18% of chromium.

Example B3:

[0055]

a) 500 g of 1,2-ethanediol are added at 25°C to 300 g of water and stirred for 10 minutes until completely dissolved. Thereafter, 200 g of butane-1,4-diol are added and stirring is effected for a further 10 minutes. The product is a colourless liquid.

b) 40% of water are added to 35 kg of pelt (from 6 to 7 mm, Brazilian zebus) in a drum, 4.2% of sodium chloride are added and a waiting period of 10 minutes is allowed. Thereafter, 0.5% of formic acid is added and the pelt is treated for one hour. 1% of the mixture according to a) is then added and allowed to act on the pelt for 1.5 hours. The pH of the liquor is 4.2. 5% of chromium sulphate having a basicity of 33% is then added and tanning is effected for 3 hours. A further 0.8% of sodium chloride is then added and treatment is effected overnight. Heating to 44°C is then effected and the liquor is kept at this temperature for 12 hours. The pH is then 4.0-4.1. The liquor is discharged and the tanned hide is washed with water. The hide has been completely tanned. The liquor contains only 0.12% of chromium.

Example B4:

[0056]

a) 100 g of hexane-1,6-diol (water content about 0.1%) are melted at 50°C in a closed glass flask. In a second glass flask, 100 g of glucose (water content about 1.0%) and 100 g of water are stirred at 50°C until the glucose has completely dissolved. Cooling to 30°C is then effected. The molten hexanediol is then added to the solution and stirring is effected for a further 10 minutes. 700 g of propane-1,2-diol are then added and stirring is effected for a further 10 minutes at 25 - 30°C. A colourless and slightly viscous product is obtained.

b) 40% of water are added to 35 kg of pelt (Swiss bulls) in a drum, 4% of sodium chloride are added and a waiting period of 10 minutes is allowed. Thereafter, 0.5% of formic acid is added and the pelt is treated for one hour. 1.5% of the mixture according to a) is then added and allowed to act on the pelt for 1.5 hours. The pH of the liquor is 4.0. 5.5% of chro-

mium sulphate having a basicity of 33% is then added and tanning is effected for 6 hours. Heating to 44°C is then effected and the liquor is kept at this temperature for 12 hours. The pH is then 3.8-3.9. The liquor is discharged and the tanned hide is washed with water. The hide has been completely tanned. The liquor contains only 0.20% of chromium.

Example B5:

[0057] 40% of water are added to 30 kg of unsplit pelt (Swiss bulls) in a drum, 4% of sodium chloride are added and a waiting period of 10 minutes is allowed. Thereafter, 0.5% of formic acid is added and the pelt is treated for one hour. 1.5% of the mixture according to example A1 are then added and allowed to act on the pelt for 1.5 hours. The pH of the liquor is then 4.5. Thereafter, 5.5% of chromium sulphate having a basicity of 33% are added and tanning is effected for 12 hours. Heating to 44°C is then effected and the liquor is kept at this temperature for 12 hours. The pH is then 3.8-3.9. The liquor is discharged and the tanned hide is washed with water. The hide is completely tanned. The liquor contains only 0.4% of chromium.

Example B6:

[0058]

a) 150 g of α-D-Glucose is added at 50°C to 100 g of water and then stirred until the glucose is completely dissolved. The temperature is reduced to 30°C, 100g of 1,2-propylene glycol methyl ether are added and stirring is effected for 10 minutes. Thereafter, 700 g of 1,2-propanediol (water content about 0.2%) are added and stirring is effected for a further 10 minutes. A colourless and liquid product is obtained.

b) 40% of water are added to 50 kg of pelt (Swiss bulls) in a drum, 4% of sodium chloride are added and a waiting period of 10 minutes is allowed. Thereafter, 0.5% of formic acid is added and the pelt is treated for one hour. 1% of the mixture according to a) is then added and allowed to act on the pelt for 1.5 hours. The pH of the liquor is 4.3. 6% of chromium sulphate having a basicity of 33% is then added and tanning is effected for 6 hours. A further 1% of sodium formate is then added. Heating to 44°C is then effected and the liquor is kept at this temperature for 12 hours. The pH is then 3.9-4.1. The liquor is discharged and the tanned hide is washed with water. The hide has been completely tanned. The liquor contains only 0.28% of chromium.

Claims

1. A process for tanning of unpickled pelts and without increasing the basicity of the liquor by the action of basic chromium(III) salts in an aqueous liquor, which is **characterized in that**

   (a) either an effective amount of at least one nonsaccharide, aliphatic polyol is added to the aqueous liquor, the pelt is pretreated and then the chromium salt is added and allowed to act, or
   (b) an effective amount of at least one aliphatic, nonsaccharide polyol and a basic chromium salt are added separately but simultaneously to the liquor and allowed to act on the pelt.

2. A process according to claim 1, **characterized in that** the chromium salts have a Schorlemmer basicity of from 25 to 50%.

3. A process according to claim 1, **characterized in that** the aliphatic polyols contain from 2 to 30 carbon atoms and optionally oxygen atoms and from 2 to 12 hydroxyl groups.

4. A process according to claim 1, **characterized in that** the polyol is a diol of the formula $HO\text{-}C_nH_{2n}\text{-}OH$, in which n is a number from 2 to 18.

5. A process according to claim 4, **characterized in that** n is a number from 2 to 6.

6. A process according to claim 1, **characterized in that** the pH of the liquor at the time of the addition of a polyol or of a chromium salt is from 3 to 8.

7. A process according to claim 1, **characterized in that**, in the process stage (a) or (b), a fungicide is additionally introduced.

8. A process according to claim 1, **characterized in that** the added amount of chromium salts is from 1 to 8% by weight of chromium trioxide (Cr_2O_3), based on the weight of the pelt.

9. A process according to claim 1, **characterized in that** the amount of polyols is at least 0.1% by weight, based on the weight of the pelts.

10. A process according to claim 1, **characterized in that** the amount of polyols is from 0.5 to 5% by weight.

11. A process according to claim 1, **characterized in that**, in the process stage (a) or (b), a fungicide, a monoalkyl ether of a glycol, or a fungicide and a monoalkyl ether of a glycol is additionally introduced.

12. Use of at least one nonsaccharide, aliphatic polyol, optionally together with the monoalkyl ether of a diol, for improving the penetration of basic chromium salts

and optionally additionally of fungicides in the tanning of unpickled pelts in weakly acidic, aqueous solution.

Patentansprüche

1. Verfahren zum Gerben von ungepickelten Blössen und ohne Abstumpfen der Flotte durch Einwirkung von basischen Chrom(III)salzen in wässriger Flotte, **dadurch gekennzeichnet, dass** man

   (a) entweder der wässrigen Flotte eine wirksame Menge wenigstens eines nicht-saccharidischen aliphatischen Polyols zugibt, die Blösse vorbehandelt und dann das Chromsalz zugibt und einwirken lässt, oder
   (b) eine wirksame Menge wengistens eines aliphatischen, nicht-saccharidischen Polyols und ein basisches Chromsalz getrennt, aber gleichzeitig zur Flotte gibt und auf die Blösse einwirken lässt.

2. Verfahren gemäss Anspruch 1, **dadurch gekennzeichnet, dass** die Chromsalze eine Basizität nach Schorlemmer von 25 bis 50% aufweisen.

3. Verfahren gemäss Anspruch 1, **dadurch gekennzeichnet, dass** die aliphatischen Polyole 2 bis 30 Kohlenstoffatome und gegebenenfalls Sauerstoffatome, sowie 2 bis 12 Hydroxygruppen enthalten.

4. Verfahren gemäss Anspruch 1, **dadurch gekennzeichnet, dass** es sich bei dem Polyol um ein Diol der Formel HO-C_nH_{2n}-OH handelt, worin n für eine Zahl von 2 bis 18 steht.

5. Verfahren gemäss Anspruch 4, **dadurch gekennzeichnet, dass** n für eine Zahl von 2 bis 6 steht.

6. Verfahren gemäss Anspruch 1, **dadurch gekennzeichnet, dass** der pH-Wert der Flotte zum Zeitpunkt der Zugabe eines Polyols oder eines Chromsalzes 3 bis 8 beträgt.

7. Verfahren gemäss Anspruch 1, **dadurch gekennzeichnet, dass** in den Verfahrensstufen (a) oder (b) zusätzlich ein Fungizid zugegeben wird.

8. Verfahren gemäss Anspruch 1, **dadurch gekennzeichnet, dass** die zugegebene Menge an Chromsalzen 1 bis 8 Gew.-% Chromtrioxid (Cr_2O_3) beträgt, bezogen auf das Gewicht der Blösse.

9. Verfahren gemäss Anspruch 1, **dadurch gekennzeichnet, dass** die Menge an Polyolen mindestens 0,1 Gew.-% beträgt, bezogen auf das Gewicht der Blösse.

10. Verfahren gemäss Anspruch 1, **dadurch gekennzeichnet, dass** die Menge an Polyolen 0,5 bis 5 Gew.-% beträgt.

11. Verfahren gemäss Anspruch 1, **dadurch gekennzeichnet, dass** in den Verfahrensstufen (a) oder (b) zusätzlich ein Fungizid, ein Monoalkylether eines Glykols, oder ein Fungizid und ein Monoalkylether eines Glykols zugegeben wird.

12. Verwendung von wenigstens einem nicht-saccharidischen, aliphatischen Polyol, gegebenenfalls zusammen mit dem Monoalkylether eines Diols zur Verbesserung der Penetration basischer Chromsalze und gegebenenfalls zusätzlich von Fungiziden beim Gerben von Blössen in schwach saurer, wässriger Lösung.

Revendications

1. Procédé de tannage de peaux non picklées sans augmenter la basicité de la liqueur par l'action de sels de chrome(III) basiques dans une liqueur aqueuse, qui est **caractérisé en ce que**

   (a) une quantité efficace d'au moins un polyol aliphatique non saccharide est ajoutée à la liqueur aqueuse, la peau est prétraitée, puis le sel de chrome est ajouté et laissé agir, ou
   (b) une quantité efficace d'au moins un polyol aliphatique non saccharide et un sel de chrome basique sont ajoutés séparément mais simultanément à la liqueur et laissés agir sur la peau.

2. Procédé selon la revendication 1, **caractérisé en ce que** les sels de chrome ont une basicité de Schorlemmer de 25 à 50 %.

3. Procédé selon la revendication 1, **caractérisé en ce que** les polyols aliphatiques contiennent de 2 à 30 atomes de carbone et éventuellement des atomes d'oxygène et de 2 à 12 groupes hydroxyle.

4. Procédé selon la revendication 1, **caractérisé en ce que** le polyol est un diol de formule HO-C_nH_{2n}-OH, dans laquelle n est un nombre de 2 à 18.

5. Procédé selon la revendication 4, **caractérisé en ce que** n est un nombre de 2 à 6.

6. Procédé selon la revendication 1, **caractérisé en ce que** le pH de la liqueur au moment de l'ajout d'un polyol ou d'un sel de chrome est de 3 à 8.

7. Procédé selon la revendication 1, **caractérisé en ce qu'**un fongicide est également introduit à l'étape de procédé (a) ou (b).

8. Procédé selon la revendication 1, **caractérisé en ce que** la quantité ajoutée de sels de chrome est de 1 à 8 % en poids de trioxyde de chrome (Cr_20_3), par rapport au poids de la peau.

9. Procédé selon la revendication 1, **caractérisé en ce que** la quantité de polyols est d'au moins 0,1 % en poids, par rapport au poids des peaux.

10. Procédé selon la revendication 1, **caractérisé en ce que** la quantité de polyols est de 0,5 à 5 % en poids.

11. Procédé selon la revendication 1, **caractérisé en ce qu'**un fongicide, un éther monoalkylique d'un glycol, ou un fongicide et un éther monoalkylique d'un glycol sont également introduits à l'étape de procédé (a) ou (b).

12. Utilisation d'au moins un polyol aliphatique non saccharide, éventuellement avec l'éther monoalkylique d'un diol, pour améliorer la pénétration de sels de chrome basiques et éventuellement également de fongicides dans le tannage de peaux non picklées dans une solution aqueuse faiblement acide.

REFERENCES CITED IN THE DESCRIPTION

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